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Effect of Nafion dispersion solvent on the interfacial properties between the membrane and the electrode of a polymer electrolyte membrane-based fuel cell

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ABSTRACT

A new Nafion binder solution was prepared using a different organic solvent, dimethylacetamide (DMAc), and applied to a polymer electrolyte membrane-based fuel cell. Wide angle X-ray diffraction (WAXD), electrochemical impedance spectroscopy (EIS), and polarization of the fuel cell were carried out to determine the crystallinity of the Nafion binder film, the cell resistance, and the fuel cell performance. This new Nafion binder film, which was created using a homemade Nafion solution containing DMAc, dissolved slower than a recast Nafion film that was made using a commercial Nafion solution in methanol (2 M). It was found that the slow dissolution of the homemade Nafion binder film was due to a more highly developed crystalline morphology, which can lead to good structural integrity in the catalyst layer for long-term operation of the fuel cell. The micellar structure of Nafion in the commercial Nafion binder solution is broken by new organic solvent, which leads to higher physical chain entanglement between the Nafion membrane and the Nafion binder during preparation of the membrane/electrode assembly (MEA), thereby improving the interfacial stability between the membrane and the electrode and providing long-term stability of the fuel cell.

1. Introduction

A Nafion solution is conventionally used as a binding material in the catalyst layer of fuel cells [1] to integrate the platinum (Pt) catalyst, suppress Pt catalyst aggregation, create a proton conduction pathway in the catalyst layer, and improve the interfacial adhesion between the membrane and the electrode. It is well-known that Nafion can increase the electrochemically active surface area (EAS) by enhancing the Pt dispersion in the catalyst layer [2]. Additionally, it can decrease the cell resistance by increasing the proton conductivity in the electrode [2] and improving the interfacial adhesion between the membrane and the electrode. These factors lead to better performance of fuel cells.

Recently, it has been determined that the long-term stability of the membrane/electrode assembly (MEA) is one of the most important issues in the commercialization of fuel cells. The life-time of a fuel cell is affected by the degradation of materials, such as the catalyst, the polymer electrolyte, the gas diffusion layer, and the bipolar plate [3]. Additionally, it has been found that interfacial delamination between the membrane and the electrode is one reason for the performance loss [4–6].

This performance loss is mainly caused by the dimensional change of the membrane and the dissolution of the Nafion binder or the Pt catalyst. The large change in the dimensions of the membrane may cause interfacial delamination because such a dimensional change would be much smaller in the electrode. Investigation of an X-ray photoelectron spectroscopy (XPS) data showed that the content of fluorine atom gradually decreased during the long-term operation of the fuel cell due to the degradation of Nafion [7,8]. In addition, because the direct methanol fuel cell (DMFC) is usually operated with a high water flow rate at a high temperature (around 70 °C), dissolution of the binder is expected because of its high solubility and low crystallinity [9,10]. The Nafion binder membrane also has slightly lower proton conductivity than the conventional Nafion membrane because of the reduced formation of sulfonic acid group clusters in the membrane morphology [11], which may decrease the proton conductivity in the electrode and increase the resistance of the fuel cell. All of these factors can deteriorate the initial performance and long-term stability of the polymer electrolyte membrane-based fuel cell.

To solve these problems, the development of a new binding material is required. The new material should have substantial chain flexibility to enhance the interfacial stability between the membrane and the electrode through the inter-penetration of the polymer chains. The polymer chains should also have a high packing density to prohibit Nafion dissolution in the catalyst layer because of the high crystallinity. To obtain these properties in the binding material, a conventional Nafion solution was modified in this study by using an alternative solvent. The conventional Nafion binder is dispersed in a water/alcohol mixture to create micelles. To break down the micellar structure of Nafion [12], recast Nafion was re-dissolved in dimethylacetamide (DMAc) for this study. It has been known that DMAc is a good dispersion solvent for

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unsupported Pt catalysts [13] and that it improves the proton conductivity of the cast membrane by interacting with the polymer [14].

To improve the interfacial stability and long-term stability of a DMFC, the objective of this study was to make a new binder material dispersed in this alternative solvent. In addition, the properties and the performance of a fuel cell containing the new electrode, which was created through the introduction of this new binder, were analyzed.

2. Experimental

2.1. Preparation of the new Nafion solution

A conventional Nafion solution (5 wt.%) was purchased from DuPont. Nafion films were prepared by casting the Nafion solution onto a Pyrex petri dish and evaporating the solvent at 80 °C. The recast Nafion films were soaked in water and then peeled off the petri dish. After the water was removed from the surface of the recast Nafion films, they were kept at 80 °C in a vacuum oven for 24 h. The dried recast Nafion films were dissolved in DMAc, at a Nafion concentration of 5 wt.%.

Dissolution of the Nafion binder film was carried out in accordance with procedures reported elsewhere [10,11,15]. The dried Nafion films were weighed and stirred in a methanol solution (2 M) for 24 h and then sonicated for 12 h. The residual solids were then filtered and dried in a vacuum oven overnight. The extent of dissolution was calculated by comparing the weight of the films before and after the test.

Dissolution of the Nafion binder in the electrode was performed in a similar fashion to the dissolution test of the Nafion binder film. The electrodes were weighed and sonicated in an ethanol/water (50/50) mixture for 12 h. The residual solids were filtered and dried in a vacuum oven overnight. Dissolution of Nafion in the electrode was confirmed by the weight difference before and after the test.

2.2. Preparation of the MEA

The active cathode material was an unsupported Pt black catalyst, and the anode catalyst was a PtRu black catalyst. The catalyst inks were prepared by dispersing the catalyst and one of the two (conventional and homemade) types of Nafion solutions. To control the viscosity of the inks, a small amount of isopropyl alcohol (IPA) or DMAc was added to the conventional and homemade Nafion ink slurries, respectively. In this study, the Nafion binder content of the cathode was set at 7 wt.%, and the amount of Nafion binder in the anode was 15 wt.%.

The electrodes were prepared using a brushing technique. The amount of catalyst loaded in the electrode was 4 mg cm^{-2}. The MEAs were prepared by hot-pressing the electrodes onto a Nafion 117 membrane at 130 °C for 3 min with a pressure of 800 psi.

2.3. Unit cell operation

The MEAs were characterized with a 2 cm^2 single cell after they were installed in the DMFC test fixtures and connected to a test station that was equipped with an electric load. The cell temperature was maintained at 30 °C, and oxygen and methanol (2 M) were supplied to the cathode and anode, respectively.

2.4. Electrochemical measurements

Cyclic voltammetry (CV) measurements of the DMFC were conducted at 30 °C on single cell fixtures with a geometric area of 2 cm^2 to determine the EAS. The measurements were based on hydrogen and nitrogen at the counter electrode (anode) and working electrode (cathode), respectively, with a potential range of 0.01 to 1.2 V vs. RHE maintaining a sweep rate of 10 mV s^{-1}. The EAS of the electrode was determined by measuring the charge required for hydrogen desorption from the Pt catalyst.

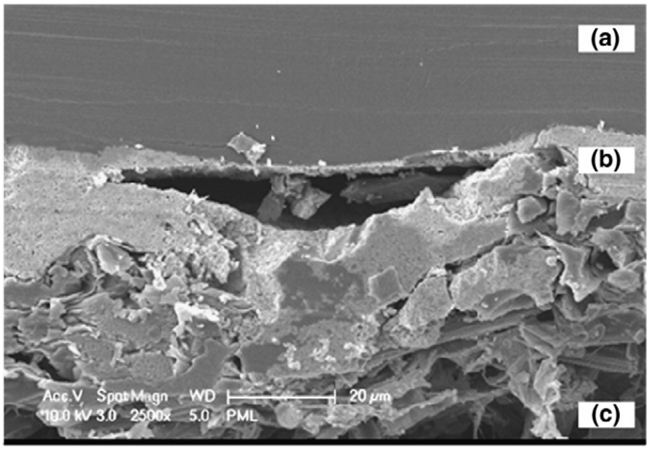

Fig. 1. The typical interface between the membrane and the electrode after long-term operation of the fuel cell (720 h) using (a) a Nafion 117 membrane, (b) a catalyst layer and (c) carbon paper.

To measure the resistance in the fuel cell, a Solartron Analytical 1470 Cell Test System, controlled by commercial software (ZView 2), was used with a perturbation amplitude of 10 mV and a frequency typically ranging from 0.05 to 10,000 Hz.

2.5. Morphology characterization

The surfaces of the electrodes were examined with a Phillips scanning electron microscope at an accelerating voltage of 10 kV. The crystalline structure of the recast Nafion film was identified by the X-ray diffraction method using a Rigaku D/max-rc (12 kW), equipped with a rotating Cu anode and a monochromator with a scanned range of 10°–20° (2θ). Before X-ray analysis, the recast Nafion film was dried at 90 °C for 72 h in a vacuum oven.

3. Results and discussion

3.1. Characterization of the Nafion binder

A fresh MEA was operated at 30 °C with excess fuel in a DMFC. The cell performance was determined by measuring the polarization curve and the constant current discharge for 720 h of operation. After long-term operation of the fuel cells, interfacial delamination was found between the membrane and the electrode, as shown in Fig. 1. This delamination was expected because of the dimensional change of the membrane and the dissolution of the binder or catalyst. Table 1 shows the change in the dimensions of the Nafion 117 membrane in a deionized water chamber at 20 and 70 °C. The Nafion membrane changed significantly, even at a conventional temperature (70 °C) for polymer membrane-based fuel cell operation. Therefore, it is generally expected that this large change in membrane dimensions might cause interfacial delamination between the membrane and the electrode because the dimensional change in the electrode is much less.

Table 1
The dimensional change of a Nafion 117 membrane in a DI water chamber at 20 and 70 °C.

	Dimensional change in DI water (%)	
Temperature (°C)	20.0	70.0
ΔL (linear)	13.1	17.4
ΔT (thickness)	13.1	17.4
ΔV (volume)	35.6	62.0

ΔV was calculated by multiplying $\Delta L^2 x \Delta T$.